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Complex Impedance Studies Of Proton-Conducting Membranes

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Complex impedance studies have been carried out on Dow 800, Dow 1000 and Nafion 117 membranes at various water contents and a variety of temperatures and pressures. At room temperature and pressure a gradual decrease in electrical conductivity with decreasing water content is observed. Apparent activation volumes as large as 54 cm^3/mol are obtained. In addition, there is a tendency for smaller equivalent weights (same side chains) or larger side chains to have larger activation volumes. Additionally, ambient-pressure, variable-temperature ^2H T_1 and linewidth measurements imply a heterogeneous environment of the water molecules. Proton pulsed field gradient NMR studies in saturated Dow membranes verify the expectation that ionic conductivity is determined primarily by diffusion of water molecules.

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Abstract

Complex impedance studies have been carried out on Dow 800, Dow 1000 and Nafion 117 membranes at various water contents and a variety of temperatures and pressures. At room temperature and pressure a gradual decrease in electrical conductivity with decreasing water content is observed. Apparent activation volumes as large as 54 cm^3/mol are obtained. In addition, there is a tendency for smaller equivalent weights (same side chains) or larger side chains to have larger activation volumes. Additionally, ambient-pressure, variable-temperature ^2H T_1 and linewidth measurements imply a heterogeneous environment of the water molecules. Proton pulsed field gradient NMR studies in saturated Dow membranes verify the expectation that ionic conductivity is determined primarily by diffusion of water molecules.

Keywords: Electrical Conductivity, Polymer Electrolytes, Proton Conducting Membranes, Activation Volume, High Pressure

Chemical Compounds: sulfonated fluorocarbons

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1. Introduction

The electrical conductivity of sulfonated fluorocarbons is of interest because they are proton conductors when they contain water. While many studies of the electrical conductivity in these types of material have been carried out [1-7 and refs. therein], relatively little work has been reported on the effect of high pressure on the conductivity. The reason for carrying out pressure studies is that insight into the proton transport mechanism can be gained. In previous papers [1,3,5], the authors have presented some results for the effect of high pressure on the electrical conductivity and proton, deuteron and oxygen-17 NMR spin-lattice relaxation times (T_1) of various equivalent weight Nafion materials. In an attempt to further elucidate the effects of the side chains, many of those experiments have been extended to Dow 800 and Dow 1000, which have shorter side chains than the Nafion materials. The results are reported in the present paper.

2. Experimental Details

All studies were carried out on Dow 800 and Dow 1000 (equivalent weights 800 and 1000, respectively) manufactured by Dow Corporation. The details of the sample pretreatment and configuration for measurement are the same as those used previously for Nafion materials [1]. In the present case, various relative humidities were achieved in a glove box with the atmosphere controlled by an ETS Model 514 Automatic Humidity Controller using an ETS 5612C Ultrasonic Humidification System. The wt-% of water in the samples for the atmospheric

pressure measurements was measured in situ and was calculated by dividing the change in mass by the mass of the dry samples. The high pressure electrical conductivity measurements were carried out as described previously for the Nafion materials [1].

The complex impedance of the samples, $Z^*= Z'-jZ''$, was determined using a CGA-83 Capacitance bridge (10-10^5 Hz), a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer or a 1255 Solartron High Frequency Response Analyzer connected to a Solartron 1296 Dielectric Interface.

^2H linewidth and T_1 measurements were performed upon D_2O saturated Dow 800 at 46 MHz with a Chemagnetics CMX 300 NMR spectrometer. For the T_1 measurements, an inversion recovery sequence was employed. An inverting pulse width of 14ms was used. ^1H pulsed field gradient (PFG)-NMR diffusion measurements (300 MHz) were performed upon Dow 800 with 31.7% water uptake and Dow 1000 with 7% water uptake. The pulse field gradient echo technique was employed, in which a $\pi/2$ resonant rf pulse is applied at time zero, a π pulse at time τ, and a spin echo is found at time 2τ. A square shaped field gradient pulse with amplitude characterized by G and duration δ is applied between the two rf pulses. A second identical gradient pulse follows the pulse at time Δ after the first one. The echo amplitude will be attenuated by an amount determined by how much the spins have changed their positions in G in the interval Δ. Experimental parameters were typically: δ = 2~10ms, Δ = 10~20ms, and G = 0.2~1.2 T/m.

3. Results And Discussion

3.1. Electrical Conductivity vs. Water Content

The complex impedance diagrams for the Dow membranes are similar to those observed for the various Nafions [1]. In general, an impedance arc, attributable to the bulk properties of the material, is observed at the highest

frequencies. In addition, a slanted line, due to electrode effects, is observed at the lowest frequencies. The data were transformed to the electrical conductivity, σ, using techniques described elsewhere [1].

The results for the variation of the electrical conductivity with water content are shown in figs. 1a and 1b. Fig. 1a includes some previously published work [1,8] for Nafion 117 and shows that the electrical conductivity decreases relatively smoothly as the water content decreases. (It is apparent from fig. 1a that the electrical conductivity results of Zawodzinski et al. for intermediate water contents [8] are slightly higher than those of the present work.) There is not much difference between the materials when compared via water content in wt-% though there is a tendency for the electrical conductivity to be highest for Dow 800. However, as is apparent from fig. 1b, the difference between the materials becomes more obvious when plotted vs. λ, the number of waters per sulfonate. Dow 800 exhibits the highest conductivity followed by Nafion 117 and then Dow 1000. That Dow 800 has a larger conductivity than Dow 1000 for a given λ is attributable to the concentration of charge carriers since a smaller equivalent weight will have more water per unit volume. That σ for Nafion 117 is between the two materials is interesting. Since Nafion 117 has a larger equivalent weight (1100) than either Dow material, it would be expected to have the lowest σ. The higher than expected conductivity for Nafion 117 is probably attributable to the different side chains for that material. Of course, the morphology of the films must also be considered.

3.2. Electrical Conductivity vs. Pressure

Plots of the electrical conductance vs. pressure are similar to those observed previously for Nafion 117 [1]. The pressure derivative of the conductance was converted to the pressure derivative of the electrical conductivity using the equation

and estimated value of χ_T given elsewhere [1]. Finally, the activation volume was calculated from the pressure variation of the electrical conductivity via:

$$\Delta V = -kT\,[\partial \ln\sigma/\partial p]_T. \qquad (1)$$

The results of the experiments and calculations are given in Table 1.

One interesting result is that the activation volumes for low water content Dow 1000 and Nafion 117 are about 50 cm^3/mol. This value is very large for proton conductivity and confirms the central role of segmental (presumably side chain) motions in the electrical conductivity of these materials at low water content. The reason is that the very large values are on the order of the values observed for typical solvent-free polymer electrolytes where it is clear that segmental motions are responsible for ionic conductivity [9].

Next, the activation volume decreases as water content increases. Correspondingly, the electrical conductivity increases. In fact, an interesting result is obtained when the activation volumes are plotted vs the electrical conductivity as shown in fig. 2. There appears to be an exponential relationship between the activation volume and the electrical conductivity, at least in the range of medium to low water content. For example, the data for Dow 1000 can be extremely well represented by:

$$\sigma = 0.025 \exp(-\Delta V/2.69) \qquad (2)$$

Further, the values of ΔV for Dow 800 tend to be larger than those for Dow 1000 and both are smaller than those for Nafion 117. These results show that, for a given side chain, ΔV is larger for a smaller equivalent weight. In addition, ΔV appears to be larger for larger side chains (Nafion 117).

All of these results can be explained qualitatively in terms of free volume. Specifically, it has recently been pointed out that since ΔV represents the volume change of the material associated with ion motion and since the free volume represents the volume already available for ion motion, greater free volume

requires smaller changes (ΔV) and vice versa [10]. Consequently, the fact that ΔV for Dow 800 is larger than for Dow 1000 is explained if the free volume for Dow 800 is smaller. This is reasonable since it is expected that greater space-filling will occur for a smaller equivalent weight. Next, the result that Nafion 117 has the largest activation volume is explained if it has the smallest free volume. Again, this is reasonable since greater space-filling could occur for larger side chains. Of course, the latter result is less definitive because the equivalent weight for Nafion 117 (1100) is larger than for either Dow material. It will be of interest to extend the measurements on Nafion 105 to lower water contents and to study intermediate water concentrations for the other materials so that a detailed, direct comparison between long and short side-chain materials can be made at the same equivalent weights.

3.3. NMR Results

^2H NMR lineshapes gathered for the D_2O saturated Dow 800 sample do not display the characteristic powder pattern divergences for spin = 1 nuclei, even at the lowest temperatures at which the measurement was conducted. Evidently, dipolar interactions and distributions in quadrupolar parameters as well as residual molecular motion are large enough to render the divergences unresolvable. This typically indicates a large degree of structural variation in the immediate environment of the water molecules. The ^2H linewidth is observed to increase as the temperature is lowered, until about 180K where the resonance becomes immeasurable due to lifetime broadening (fig. 3).

^2H T_1 measurements for Dow 800 are comparable to results reported earlier for hydrated Nafion membranes [7]. Assuming that ^2H relaxation is predominantly dipolar, a BPP interpretation to these data yield an activation energy of about 0.3eV. This approach is somewhat artificial, since the real relaxation mechanism

involves a distribution of interactions (including a quadrupolar contribution). However, it is interesting to compare this result with 0.27eV obtained for a Nafion membrane containing 18.3 wt.% D_2O.

Room temperature ^1H PFG-NMR measurements for both Dow 800 (31.7 wt.% water uptake) and Dow 1000 (7 wt.% water uptake) have been carried out. The results yield self-diffusion coefficients of 4.2×10^{-6} cm^2/s and 7.4×10^{-7} cm^2/s for the Dow 800 and Dow 1000 materials respectively. These values are comparable to those determined for Nafion 117 with similar water content. They are also consistent with the electrical conductivity results presented in fig. 1, where low water contents yield lower conductivities in that it is confirmed that the protonic conductivity of the membrane at high water concentration is strongly dependent on the water molecular diffusivity.

4. Conclusions

In summary, several results have been obtained via complex impedance studies of Dow 800, Dow 1000 and Nafion 117 membranes. At room temperature and pressure a gradual decrease in electrical conductivity with decreasing water content is observed. For the low water content materials the variation with pressure is large giving rise to apparent activation volumes as large as 54 cm^3/mol. In addition, there is a tendency for smaller equivalent weights (same side chains) or larger side chains to have larger activation volumes. These results are explained in terms of free volume. Additionally, ^1H pulsed field gradient NMR support the electrical measurements. Variable-temperature linewidth studies indicate a large degree of structural variation in the D_2O environments.

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Table I. Effect of pressure on the electrical conductivity for sulfonated fluoropolymer membranes.

T	σ	Water Content	λ	$\frac{\partial \ln G}{\partial p}$	$\frac{\chi_T}{3}$	$\frac{\partial \ln \sigma}{\partial p}$	ΔV
(K)	(S/cm)	(wt-%)		$(GPa)^{-1}$	$(GPa)^{-1}$	$(GPa)^{-1}$	(cm^3/mol)
Dow 800							
285.1	$\approx 5.6 \times 10^{-6}$	0.066	0.03	-12.1	0.1	-12.0	28.6
294.6	1.33×10^{-5}	0.066	0.03	-10.4	0.1	-10.3	25.3
318.1	$\approx 1.1 \times 10^{-4}$	0.066	0.03	-7.86	0.1	-7.76	20.5
296.6	3.28×10^{-3}	3.2	1.4	-2.45	0.1	-2.35	5.80
296.6	1.90×10^{-2}	10.9	4.8	-1.29	0.1	-1.19	2.93
Dow 1000							
296.6	1.37×10^{-9}	≈0	≈0	-18.4	0.1	-18.3	45.1
296.6	1.34×10^{-3}	2.4	1.4	-3.26	0.1	-3.16	7.80
296.6	7.67×10^{-3}	7.2	4.0	-1.42	0.1	-1.32	3.25
296.6	2.87×10^{-2}	16.4	9.2	≈0	0.1	+0.1	-0.25
Nafion 117							
323.1	4.27×10^{-8}	≈0	≈0	-20.3	0.1	-20.2	54.3

Figure Captions

Figure 1. (a) Electrical conductivity vs. water content in wt-% for various sulfonated fluorocarbons at room temperature. The values for Nafion 117 represented by the open squares are new. For comparison, previously reported results for Nafion 117 are also included. (b) Electrical conductivity vs. λ, the number of waters per sulfonate, for various sulfonated fluorocarbons at room temperature. The values for Nafion 117 represented by the open squares are new. See fig. 1a for a legend.

Figure 2. Activation volume vs. electrical conductivity for various samples of Dow 800 and Dow 1000. For comparison, previously reported results for Nafion 117 are also included. See fig. 1a for a legend.

Figure 3. Deuteron NMR T_1 (open circles) and full width at half maximum (solid circles) vs. reciprocal temperature for water-saturated Dow 800 samples.

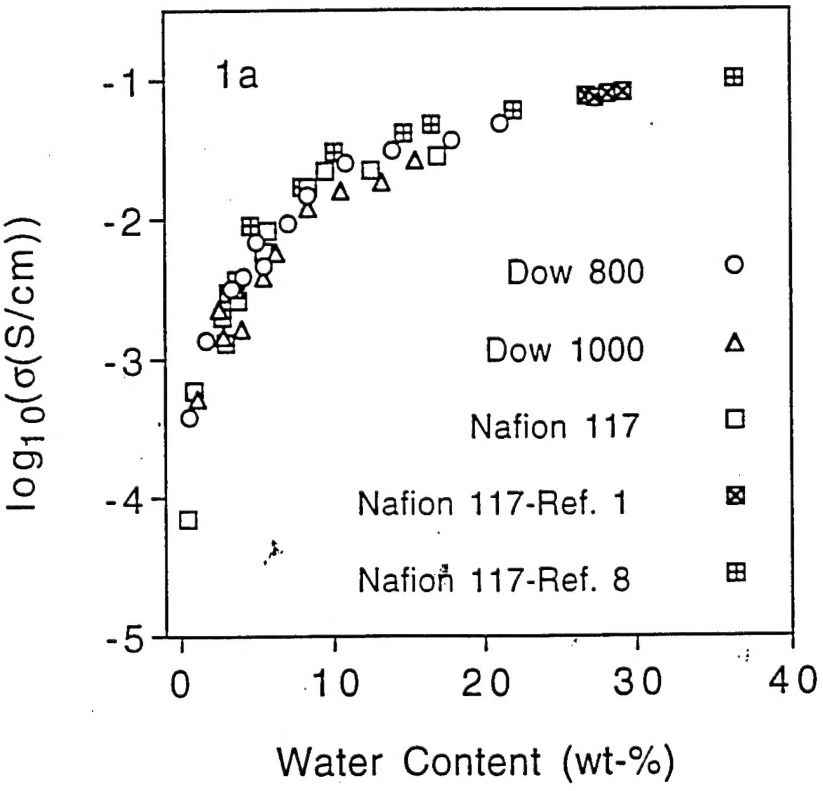

Figure 1a

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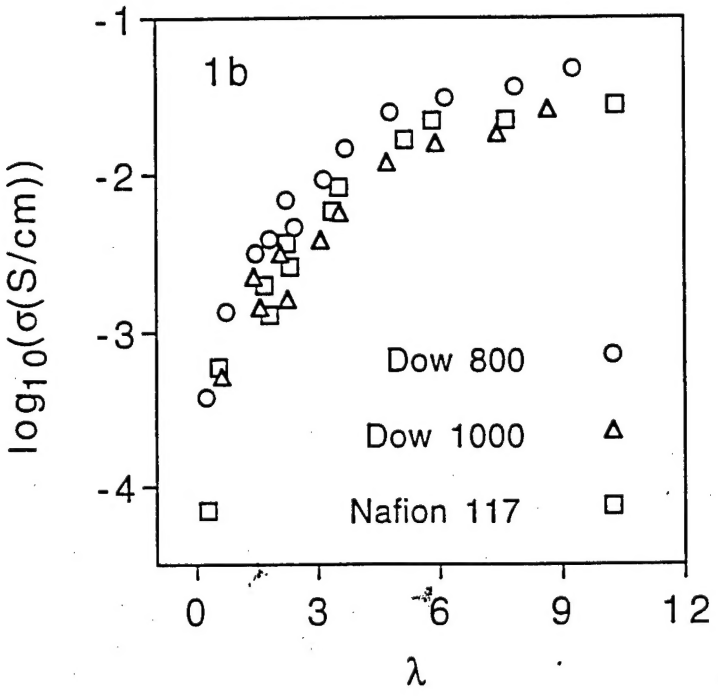

Figure 3

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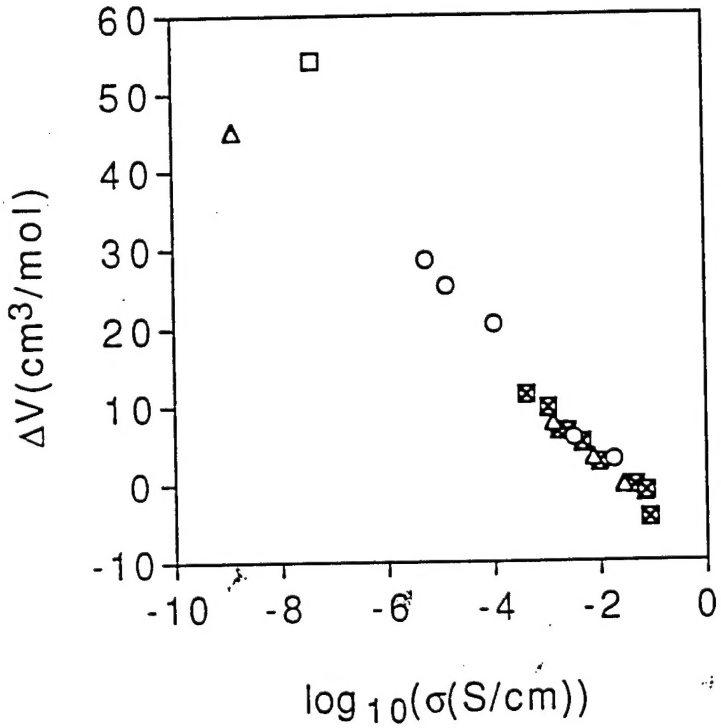

Figure 3

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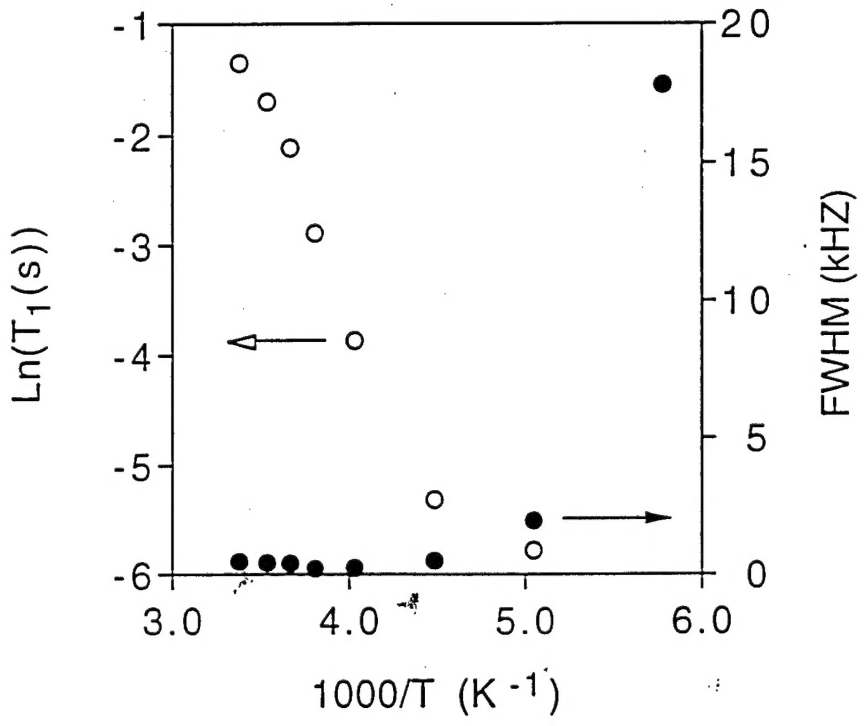

Figure 2

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